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Theoretical Study of Oxidative Addition to Platinum Metal Complexes. III. Activation of Methane, Ethane, and Propane with 16-Electron Palladium(II) and Platinum(II) Chlorocyclopentadienyl Complexes

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Abstract

Nonempirical MO methods were used to calculate the structure of the palladium(II) and platinum(II) cyclopentadienyl complexes CpMCl (M = Pd, Pt) and the reactivity of the complexes toward σ-donors (water, HCN) and alkanes R-H (methane, ethane, and propane). The 16-electron complexes, unlike isoelectronic square-planar derivatives of these metals, form strong complexes with water and hydrogen cyanide, as well as σ complexes with methane. The results of MP2 and B3LYP calculations are compared. The oxidative addition of methane to chlorocyclopentadienylpalladium(II) is a synchronous process with a low activation energy, while the reaction with the platinum analog occurs with heat evolution. The much higher exothermicity and rate of the addition reactions of these complexes compared with planar palladium and platinum complexes is explained by the fact that in the former case the coordination entity should not strongly deform during the reaction. According to MP2 and B3LYP calculations, the exothermicity of addition of small alkanes to chlorocyclopentadienylplatinum(II) falls in the order R = n-Pr ≈ i-Pr > Et > Me.